

## **6 Issues Involving Photochemical Simulation Models and the Ozone Weekend Effect**

This chapter considers selected issues relating to the use of photochemical simulation models to discern the true cause or causes of the ozone weekend effect. One of the primary uses of models is to evaluate and compare the effects on air quality of potential emission reduction strategies. Mechanistic models, such as the Urban Airshed Model and other, newer varieties, are well suited to these comparisons of relative effects, and have been used for such purposes for almost two decades. They can be used to assess the effects of emission changes associated with the weekend affect also.

However, the ARB believes strongly that models must undergo thorough performance evaluations before appropriately applying them to address various purposes like those above. The potential for compensating errors and bias can easily lead to misleading answers without a good understanding of model performance. Without rigorous model performance evaluation of multiple aerometric parameters in magnitude, time, and space, it is very possible to get “the correct answer for the wrong reasons.” Such performance evaluations are described in the ARB’s Technical Guidance Document: Photochemical Modeling.

There may be additional concerns involved with applying models to evaluate the emission changes associated with the weekend effect. Among those is the need to develop an inventory truly representative of weekend emissions, a difficult task given the complexity of the spatial, temporal, and compositional variations in the mix of emission sources on weekends and the limited amount of weekend-specific information. Most of the complexities associated with evaluating the ozone weekend effect may be addressed by paying special attention to certain aspects of the model performance evaluation, or, when possible, through model sensitivity studies. This chapter considers selected concerns related to the use of photochemical models to isolate and quantify the primary contributors to the ozone weekend effect.

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## **6.1 Technical Issues for Performance Analyses When Using Photochemical Simulation Models to Study the Causes of the Ozone Weekend Effect**

### **6.1.1 Abstract**

Photochemical simulation models are continually improved to make them more realistic and reliable. During the last 10 years, several advances have been made. Chemical mechanisms have been improved. Emission inventories have been updated and significantly improved, qualitatively and quantitatively. Vertical resolution has been increased by using more layers both below and above the mixing height. Wind fields are now more detailed and realistic. When properly applied and used in conjunction with other corroborative analysis tools, photochemical models can provide valuable insight into the contributors of the ozone weekend effect.

The ozone weekend effect involves relatively small changes in ozone concentrations in response to complex and relatively large, transient changes in emissions. For investigating the weekend effect, a modeling study must do more than properly simulate the ozone response to transient changes in emissions by day of week. Such an investigative study ought also to isolate the factors within the ozone-generating system that contribute to the ozone response. For this purpose, the performance evaluation should address the model's responses to the factors that are plausible contributors to the ozone response.

Hypotheses discussed in Chapter 3 of the Staff Report identify multiple factors as plausible contributors to the ozone weekend effect. These include an increase in the ambient VOC/NO<sub>x</sub> ratio, a change in the timing of emissions during the day, and contributions from pollutants that carry over from the previous day. Separating the effects of these factors is important because one factor may imply that regulatory NO<sub>x</sub> reductions would increase the maximum ozone concentrations while another may imply that regulatory NO<sub>x</sub> reductions would help reduce the maximum ozone concentrations. To resolve the contributions of several factors successfully, a model's performance analysis should show the model is appropriately responsive to changes in the plausible contributing factors.

Four specific points are discussed in this chapter. First, the need for an accurate weekend inventory is emphasized. Second, the performance of the chemical mechanism is discussed in relation to determining the effects of changes in the VOC/NO<sub>x</sub> ratio. Third, the importance of the simulated concentrations of pollutants above the surface is discussed in relation to the impact of pollutants that carry over aloft. Finally, the significance of realistic simulated concentrations of pollutants at the start of each modeled day is discussed in relation to the impacts of carry over and of changes in the timing of emissions.

The conclusion from this chapter is that the concerns discussed here should be carefully considered during performance evaluations for models used to investigate

the ozone weekend effect. The results of such investigations should help validate model results or lead to improvements that will enhance the ability of modeling studies to isolate and quantify the effects of the potential causes of the ozone weekend effect.

### **6.1.2 Introduction**

The ozone weekend effect is a transient effect resulting from transient changes in the relative mix, location, and timing of emissions of ozone precursors.

Photochemical simulation models are most often used to predict the effects of regulations that change emissions in a consistent (steady, proportional, across the basin) manner, rather than in a spatially and temporally variable manner as transiently occurs from a weekday through a weekend. For study of the ozone weekend effect, this implies that rigorous efforts be applied toward development of a weekend emission inventory that properly reflects the transient nature of the emissions. It also calls for a detailed performance evaluation to diagnose potential problems in the inventory and to ensure that the model is properly simulating the relevant physical processes. Without a satisfactory emission inventory and performance evaluation, a modeling study might not properly attribute portions of the ozone weekend effect to multiple factors within the ozone-generating system. For example, historical modeling performance evaluation successfully focused on the magnitude, location, and timing, of ozone peaks despite later evidence that the mobile source emissions of VOC and CO were underestimated by approximately a factor of two.

Chapter 3 in the Staff Report identifies multiple hypotheses for the factors that can contribute to the ozone weekend effect. A complete performance evaluation for modeling the ozone weekend effect should include assessments of the model's response, jointly and individually, to each of the hypothesized factors.

Four specific concerns or issues are discussed below. Each issue should be carefully considered during model application to ensure that the model does not overlook a significant cause of the weekend effect while overstating the importance of another. Examples included in the discussion are presented as illustrations of concepts rather than demonstrations of problems with present-day models.

### **6.1.3 Issue #1: Weekend emission inventory**

An accurate emission inventory is a fundamental requirement of photochemical models. Without proper characterization of the temporal, spatial, and compositional variations in the inventory, it is unreasonable to expect any model to faithfully reproduce the physical phenomena under study. Historically, most inventory efforts have focused on weekday inventories, but more refined, day-specific efforts have been undertaken in recent years. A particular challenge to study of the ozone weekend effect will be the continued development of rigorous weekend inventories

that accurately characterize the spatial and temporal (diurnal and heptdomodal) variations.

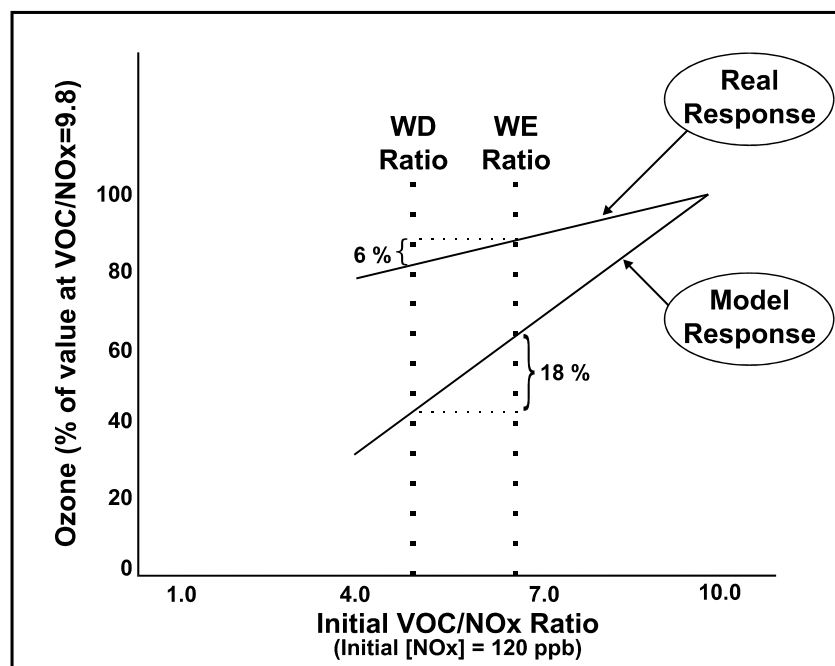
#### **6.1.4 Issue #2: Performance of chemical mechanisms**

Ambient measurements indicate that the VOC/NO<sub>x</sub> ratio does increase on weekends. This increase probably occurs because the decrease in ambient NO<sub>x</sub> concentrations on weekends is greater than the decrease in VOC concentrations. It is common in the South Coast Air Basin, for example, for ambient NO<sub>x</sub> concentrations to average 40 percent lower during the daylight hours on Sunday compared to Friday while VOC concentrations are only 25 percent lower. This implies an increase of 25 percent in the VOC/NO<sub>x</sub> ratio on Sunday compared to Friday (see Chapter 5.3).

Photochemical simulation models used to study the ozone weekend effect should perform well over the range of ambient VOC/NO<sub>x</sub> ratios and ozone precursor concentrations found in the domain of interest. Most recently developed chemical mechanisms have been extensively validated under present-day VOC/NO<sub>x</sub> ratios and precursor concentrations that commonly occur. However, a model may rely on a mechanism that has not been validated for such conditions. The importance of using a chemical mechanism validated for the conditions being examined can be seen in the following discussion of research published in 1992 that compared several older chemical mechanisms under various conditions.

A chemical mechanism that underestimates ozone formation when the VOC/NO<sub>x</sub> ratio is low but does not underestimate ozone formation when the VOC/NO<sub>x</sub> ratio is high will tend to overstate the importance of the VOC/NO<sub>x</sub> ratio as a cause of the ozone weekend effect. Figure 6.1-1 shows a hypothetical case of such a situation.

**Figure 6.1-1.** Hypothetical effect of a systematic bias due to uncertainty in the chemical mechanism used in a photochemical simulation model



A set of experiments, published in 1992, considered four older chemical mechanisms and found that all four produced simulated ozone concentrations that agreed with smog chamber results when the VOC/NO<sub>x</sub> ratio was 9.6. However, three of the four mechanisms produced simulated ozone concentrations that were ~50% too low when the VOC/NO<sub>x</sub> ratio was changed to 4.8. In both experiments, the initial NO<sub>x</sub> concentration was 100 ppb, and factors other than the VOC/NO<sub>x</sub> ratio were held constant in so far as possible. [See Figure 4 in Hess, et al., 1992.]

Assuming an approximately linear relationship, the underestimation increased by slightly more than 10% per unit change in the VOC/NO<sub>x</sub> ratio. When applied to the differing VOC/NO<sub>x</sub> ratios on weekdays and weekends, significant errors can occur. A typical VOC/NO<sub>x</sub> ratio might be 6.4 on a Sunday morning and 4.8 (25% lower) on a Friday morning. The difference in these VOC/NO<sub>x</sub> ratios is 1.6 units.

In the hypothetical example, a 6% increase in ozone is due to the increase in the VOC/NO<sub>x</sub> ratio. The model, however, indicates an 18% increase due to the increase in the VOC/NO<sub>x</sub> ratio because the chemical mechanism performs poorly.

It should be noted that the experiments discussed above do not demonstrate that three of the four mechanisms are necessarily biased. It should also be noted that the four mechanisms discussed are older mechanisms. The point here is simply to

illustrate the importance of using a chemical mechanism that has been thoroughly validated over real-world combinations of VOC/NO<sub>x</sub> ratios and NO<sub>x</sub> concentrations.

Furthermore, chemical mechanisms must be updated as new validated information regarding atmospheric reactions becomes available. Chemical mechanism updates are necessary to accurately portray the chemical processes occurring in the atmosphere and to accurately assess the impacts of perturbations to the photochemical system. For example, recent investigations indicate that chlorine chemistry could have a significant impact on ozone reactions (Knipping and Dabdub, 2000 and 2003) and that deposition of nitric acid may not completely remove NO<sub>x</sub> products from the ozone formation cycle as has been previously thought (Mochida and Finlayson-Pitts, 2000; Saliba et al., 2000). As new chemical processes that could have appreciable influence on the formation of ozone are identified and quantified, they must be included in future chemical mechanisms.

### **6.1.5 Issue #3: Model performance when simulating air quality aloft**

Developers of photochemical simulation models have increased the vertical resolution of models in recent years. It is anticipated that the use of more layers to represent the atmosphere will improve model performance in simulating concentrations aloft. In addition, wind fields have become more detailed and realistic and may improve the simulation of pollutant concentrations aloft. Models that incorporate such improvements may be more successful at simulating the vertical mixing process. Such models should be suitable for studying the contribution of “carryover” to the ozone weekend effect.

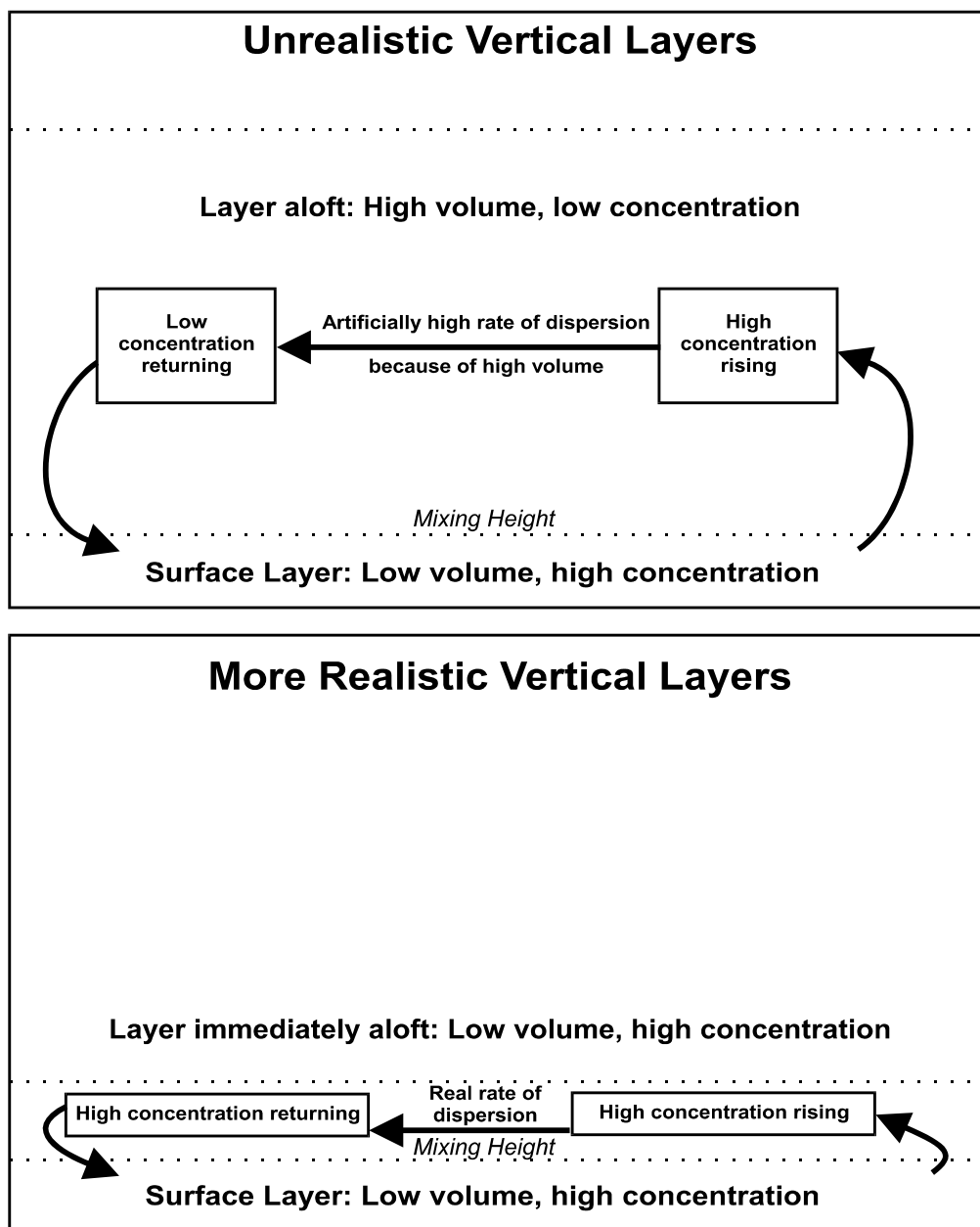
When investigating the ozone weekend effect using a photochemical simulation model, the model performance evaluation should address the simulation of air pollutant concentrations aloft (surface to 1500 m). The discussion below indicates the need for effective simulation of air quality aloft in relation to the ozone weekend effect.

#### Potential impact of the vertical structure of polluted and clean layers of air aloft

Large reservoirs of pollutants can be sequestered overnight in the atmosphere above a nighttime surface-based inversion. Such reservoirs can be 1000 meters thick beginning a few hundred feet (perhaps even less) above the ground. As these pollutants mix downward during the course of a day, they may have a marked impact on the amount of ozone measured at the surface.

Figure 6.1-2 shows how unrealistic and more realistic structures of the vertical layers in a model can produce less realistic and more realistic estimates for the impact of pollutants aloft. As the surface warms, convection takes place and warm air parcels with large amounts of pollutants rise. This causes the mixing height to rise and incorporate some of the air that previously was above the well-mixed layer.

**Figure 6.1-2 Hypothetical impact of vertical layer structure on modeled vs. real pollutant concentrations in an evolving well-mixed layer**



The unrealistic structure in Figure 6.1-, has a thin layer (low volume) at the surface and a single thick layer (high volume) aloft. Pollutants enter the surface layer, which may contain high concentrations. As the surface warms, convection causes air parcels to rise from the surface layer into the layer aloft. The pollutants that rise along with the air are dispersed by the model throughout the thick layer, though the air may actually rise only a short distance into that layer. In this situation, the air aloft is characterized by artificially low concentrations of pollutants.

When simulated concentrations of pollutants aloft are too low, the impact of carry over aloft on surface concentrations is likely to be underestimated. The simulated



concentrations at the surface will not contain appropriate contributions due to carryover. Models that operate in this or a similar manner may be ill equipped to determine the contribution of carryover to the ozone weekend effect.

When a model is used to study the causes of the ozone weekend effect, the performance evaluation should consider whether the vertical structure is likely to discount the contribution of carryover.

#### Potential for modeled meteorological fields to misrepresent vertical mixing

Even when the vertical layers in a model contain appropriate concentrations of pollutants, the meteorological field used in the model may artificially restrict/enhance vertical mixing processes. If this happens, the model may underestimate/overestimate the contribution of carryover to surface pollutant concentrations. For example, if the meteorological model predicts less mixing than actually occurred, less of the reservoir of pollutants aloft would be mixed down to impact the surface concentrations. In this case, the photochemical modeling results would underestimate the surface ozone concentrations.

When a model is used to study the ozone weekend effect, the performance evaluation should also consider whether the meteorological fields have properly represented the vertical mixing of pollutants.

#### **6.1.6 Issue #4: Model performance in establishing the initial context for each day**

Each day of an “episode” used in a modeling study begins to unfold within a context. In the real world, this context is the actual concentrations of pollutants in three dimensions throughout the domain. In the world of the model, the context is the simulated concentrations of pollutants in three dimensions throughout the domain.

Research in past decades concluded that the context at the start of a modeled day can have a significant influence on the pollutant concentrations generated by the model during the day. This research considered the influence of initial conditions and boundary conditions on the simulated pollutant concentrations that followed.

Modeling studies require the specification of initial and boundary conditions. These data are often inferred from available measured data. Scientists have found that in some cases the choice of initial conditions and boundary conditions can influence the model results significantly. Therefore, two steps are commonly taken to avoid having assumptions about initial and boundary conditions “drive the model.” Because of these steps, the influence of initial and boundary conditions is usually negligible.

First, the simulations are usually started multiple days before the day(s) of interest to allow the model to develop concentration fields that are driven by emissions, transport and chemistry. In this way, the specified initial conditions are said to “wash out.”

Second, domain boundaries may be set far away from the regions of greatest interest – more than 100 km horizontally and more than 5 kilometers vertically – to minimize the impact of the boundary conditions on the modeled pollutant concentrations.

Minimizing the impacts of initial and boundary conditions on model predictions allows the model to use the preceding day's emissions and meteorology to set the context for the following day. That is, the context on days of interest is established by the concentration fields generated by the model in response to emissions, transport, and chemistry. For example, the predicted concentration fields for a Saturday or Sunday morning are dependent on the emission estimates for the preceding days, as well as the meteorological fields and chemistry used to produce the concentration estimates. Because the model itself defines the initial context for each day, the model performance evaluation should pay special attention to the fidelity of these concentration fields.

### **6.1.7 Conclusions**

Routine performance evaluations in modeling studies might consider all or some of the issues discussed in this section. Specific attention is called to these issues, however, because they are particularly important with respect to the ozone weekend effect. Poor performance in these areas could mean that a potentially significant cause of the ozone weekend effect would be overlooked. This is particularly important for factors associated with NO<sub>x</sub> emissions because, depending on the actual conditions and factor, they can have different effects and therefore different regulatory implications.

Model-based studies of the ozone weekend effect may be used to provide important information to policy makers concerning the effectiveness of regulations reducing NO<sub>x</sub> emission. Therefore, appropriate criteria for the issues discussed above should be satisfied in the model performance evaluation.

### **6.1.8 Recommendations**

Photochemical simulation models are more quickly applied and less costly than field studies. However, a complete model performance evaluation is necessary to develop confidence that the model is able to properly simulate the significant factors thought to contribute to the ozone weekend effect.

#### Emission Inventory

A great deal of care and attention will need to be paid to development of the weekend inventories used to study the ozone weekend effect. Without this effort, it will be unreasonable to expect photochemical modeling to properly reflect the temporal, spatial, and compositional variations that may contribute to this effect.

### Chemical Mechanisms

The issue concerning chemical mechanisms is best addressed by using mechanisms which have been validated under the appropriate range of conditions present on weekdays and weekends. Since new smog chamber studies under low VOC/NO<sub>x</sub> and low NO<sub>x</sub> conditions are forthcoming, these validations should be updated as these newer data become available. As new information related to chemical reactions in the atmosphere are confirmed and quantified (e.g., chlorine atoms and nitric acid), the chemical mechanisms used in the photochemical models ought to be updated.

In addition, the existing body of data on which chemical mechanisms are based could be examined with respect to the issues discussed in this chapter.

### Vertical Mixing

The issues surrounding vertical mixing are best addressed via model performance evaluations of aloft conditions using the extensive three-dimensional aerometric datasets available from the 1997 Southern California Ozone Study (SCOS97) and 2000 Central California Ozone Study (CCOS).

In addition, field data, such as those discussed in the Recommendations in the Staff Report may be useful corroborating the modeling information. Of particular interest would be measurements of pollutants aloft that were independent of the data collected aloft during validation of the model (e.g., SCOS97 or CCOS).

### Context – Simulated pollutant concentrations in three dimensions

The ozone weekend effect may represent contributions from multiple factors. Comprehensive 3-dimensional data sets of emissions and aerometric conditions transitioning from weekday to weekend to weekday will need to be developed to properly study the effect. Performance criteria for the “context” determined by the simulated concentration field should be considered in light of the range of effects to be identified. It is not unreasonable to expect the appropriate criteria for these technical exercises to be tighter than the criteria historically suitable in most other modeling studies.

#### **6.1.9 References**

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